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Sir:

Transmitted herewith for filing is the patent application of

Inventor(s): OGAWA, Hiroshi

For: RADIATION IMAGE CONVERSION PANEL

Enclosed are:

- X A specification consisting of 28 pages  
\_\_\_ sheet(s) of \_\_\_ drawings  
X An assignment of the invention  
X Certified copy of Priority Document(s)  
X Executed Declaration X Original \_\_\_ Photocopy  
\_\_\_ A verified statement to establish small entity status under 37  
CFR 1.9 and 37 CFR 1.27  
\_\_\_ Preliminary Amendment  
X Information Disclosure Statement, PTO-1449 and reference(s)

Other \_\_\_\_\_

The filing fee has been calculated as shown below:

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Respectfully submitted,

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# RADIATION IMAGE CONVERSION PANEL

## BACKGROUND OF THE INVENTION

### Field of the Invention:

The present invention relates to a radiation image conversion panel using a stimuable phosphor.

### Description of the Related Art:

As a method which can replace conventional radiography, a radiation image conversion method using a stimuable phosphor is described, for example, in Japanese Patent Application Laid-Open (JP-A) No. 55-12145. This method utilizes a radiation image conversion panel containing a stimuable phosphor (also referred to as an accumulative phosphor sheet). In this method, radiation transmitted through a subject or emitted from an object to be examined is absorbed into the stimuable phosphor of the above-mentioned panel, and the stimuable phosphor is excited by an electromagnetic wave (stimulating ray) such as visible light or infrared light in a time sequential manner so as to allow radiation energy accumulated in the stimuable phosphor to emit as fluorescent emission (stimulated emission). Subsequently, an electric signal is obtained by photoelectrically reading the fluorescence, and based on the obtained electric signal, a radiation image of the subject or object to be examined is reproduced as a visible image.

The above-described radiation image conversion method provides an advantage that a radiation image having abundant

information can be obtained by a radiation dosage far smaller than that in conventional radiography using a combination of a radiographic film and sensitized paper. Accordingly, this method is of great value of utilization particularly in direct medical radiography such as X-ray photography used for diagnostic purposes.

The radiation image conversion panel used in the radiation image conversion method has a basic structure comprised of a support and a phosphor layer provided on one side of the support. However, the support is not necessarily needed if the phosphor layer is a self-supporting layer. Further, the surface of the phosphor layer opposite to the side at which the support is located (i.e., the surface of the phosphor layer which does not face the support) has generally a transparent protective layer to thereby protect the phosphor layer from chemical deterioration or physical impact.

Generally, the phosphor layer is comprised of a stimuable phosphor and a binder which contains and supports the phosphor in a state of dispersion. When the stimuable phosphor is irradiated with stimulating ray after having absorbed radiation such as X-rays, it exhibits the property of stimulated emission. Accordingly, the radiation transmitted through a subject or emitted from an object to be examined is absorbed in the phosphor layer of the radiation image conversion panel in proportion to the amount of the radiation, and a radiation image of the subject or the object to be examined is formed as an image of accumulated radiation energy in the radiation image conversion panel. The accumulation image can be released as

stimulated emission light by the irradiation with stimulating ray, and photoelectrically reading the stimulated emission light and converting the same into an electric signal, so that the radiation energy accumulation image can be made into a visible image.

The radiation image conversion method is, as described above, a greatly advantageous image formation method. A radiation image conversion panel used by the radiation image conversion method is desirably one having a high sensitivity and providing an image of excellent image quality (sharpness, graininess, and the like) as well as sensitized paper used by conventional radiography. The sensitivity of the radiation image conversion panel basically depends on a total quantity of stimulated emission light of a stimuable phosphor contained in the radiation image conversion panel, and the total quantity of emission light varies not only due to light emission intensity of the phosphor itself, but also due to an amount of the stimuable phosphor contained in the phosphor layer. If the amount of the stimuable phosphor contained is large, the phosphor layer absorbs a large amount of radiation such as X-rays. Therefore, the sensitivity of the panel can be made higher, and simultaneously, the image quality (particularly, graininess) of the panel improves. On the other hand, when the amount of the stimuable phosphor contained in the phosphor layer is constant, a layer thickness of stimuable phosphor grains can be made thinner as packing density of the phosphor grains becomes greater. As a result, spread of stimulating ray caused by scattering can be reduced and relatively better sharpness can be

obtained.

There has recently been increased demand for improved image quality, and therefore, a radiation image conversion panel obtained by forming a phosphor layer on a support and by compressing the phosphor layer is disclosed in JP-A Nos. 59-126299 and 59-126300. The radiation image conversion panel thus obtained allows, by compression processing of the phosphor layer, density of a stimuable phosphor in the phosphor layer to become greater than that in conventional radiation image conversion panels.

#### SUMMARY OF THE INVENTION

Even the above-described technique did not sufficiently meet the demand made in recent years for better image quality.

Particularly, if the grain size of the stimuable phosphor to be used is small, excellent graininess and sharpness can be obtained. However, the quantity of emission light decreases, and therefore, the signal-to-noise (S/N) ratio becomes adverse. In contrast, if the grain size is large, the quantity of emission light is also large. However, in this case, the graininess cannot be improved. Accordingly, it is difficult to simultaneously achieve a sufficient or optimum quantity of emission light and a high-level graininess.

Accordingly, an object of the present invention is to provide a radiation image conversion panel providing a sufficient quantity of emission light and having a high graininess. Specifically, a radiation image conversion panel in which graininess noise can be reduced

without decreasing the quantity of emission light and a radiation image of excellent image quality can be obtained.

The present inventors have focused on that the phosphor layer is divided into two or more layers having different characteristics, and further researched. As a result, they have devised the invention discussed herein.

According to a first aspect of the present invention, there is provided a radiation image conversion panel comprising at least two phosphor layers each containing a stimuable phosphor and a binder, wherein an amount (by weight) of the binder to the stimuable phosphor in uppermost phosphor layer of the phosphor layers is greater than that of the binder to the stimuable phosphor in any other phosphor layers.

According to a second aspect of the present invention, the radiation image conversion panel is constructed in such a manner that the amount (weight) of a binder to a stimuable phosphor in the uppermost layer of the phosphor layer is greater than that of the binder to a stimuable phosphor in any other phosphor layers by at least 0.5 wt%.

In the radiation image conversion panel according to the present invention, the phosphor layer is comprised of at least two layers and the amount of the binder in the uppermost layer of the phosphor layer to the stimuable phosphor is greater than that of the binder in any other layers. Therefore, at least one of layers other than the uppermost layer is allowed to have function of emitting a large

quantity of light and the uppermost layer is allowed to exhibit high graininess. As a result, the radiation image conversion panel of the present invention is excellent in emission of a sufficient quantity of light, and the graininess, and also has a desired S/N ratio.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will hereinafter be described in detail with reference to an embodiment thereof.

A radiation image conversion panel of the present invention is usually formed with a phosphor layer being provided on a support, and when necessary, a protective layer, a colored layer, an edge covering layer, and the like may be selectively provided.

Various structural parts of the radiation image conversion panel of the present invention will first be described in detail.

(Phosphor layer)

A phosphor layer contains at least a stimuable phosphor and a binder, and when necessary, various additives may be selectively added.

The phosphor layer is comprised of at least two layers, and the amount of a binder to a stimuable phosphor contained in the uppermost layer of the phosphor layer is greater than that of a binder to a stimuable phosphor contained in each of other layers than the uppermost layer. The upper most layer is a phosphor layer which is nearest to the side at which a radiation such as X-ray irradiates. Due to this structure, the graininess can be improved and graininess noise



can be reduced in the uppermost layer of the phosphor layer, which has the greatest influence on the graininess noise while maintaining a predetermined quantity of emission light in at least one of the other layers. As a result, a radiation image having excellent image quality can be obtained.

The amount of the binder to a stimuable phosphor in the uppermost layer of the phosphor layer is preferably greater than that to a stimuable phosphor in each of layers other than the uppermost layer by 0.5 percent by weight ("wt%") or more, particularly preferably 1.0 wt% or more. If the former is greater than the latter by about 100 wt% or more, there may be cases in which such adverse effect that the quantity of emitted light per thickness of the layer decreases be apt to occur.

The amount of the binder to a stimuable phosphor in each layer of the phosphor layer varies due to desired characteristics of the radiation image conversion panel, the kind of a phosphor, and the like. The amount of the binder is preferably selected from a range from 1 to 100 wt%, more preferably a range from 2.5 to 12.5 wt%.

The thickness of each layer of the phosphor layer varies due to desired characteristics of the radiation image conversion panel, the kind of a phosphor, and the like. Normally, the thickness is preferably in a range from 20 to 500  $\mu\text{m}$ , more preferably in a range from 50 to 300  $\mu\text{m}$ . Further, the thickness of each layer may be the same or different. However, when graininess is regarded as relatively more important, the thickness of the uppermost layer is increased, and

when sharpness and a quantity of emitted light are regarded as relatively more important, the thickness of the uppermost layer is decreased, thereby making it possible to control the graininess, the sharpness, and the quantity of emitted light.

The phosphor layer is comprised of at least two layers, preferably two to five layers, and more preferably two or three layers. When the phosphor layer is comprised of three layers or more, the relationship between the amounts of binders in other layers than the uppermost layer for the stimuable phosphor is not particularly limited. However, it is preferable that the amounts of binders in these layers be gradually made smaller from top to bottom.

[Stimuable phosphor]

The stimuable phosphor is, as previously described, a phosphor which exhibits stimulated emission due to stimulating ray being irradiated thereon after being irradiated with radiation. In practical terms, a phosphor which emits stimulated emission in a wavelength range from 300 to 500 nm by stimulating rays in a wavelength range from 400 to 900 nm is desirably used. Preferable examples of the stimuable phosphor include a bivalent europium-activated alkaline earth metal halide based phosphor, a cerium-activated alkaline earth metal halide based phosphor, and a cerium-activated rare earth oxyhalide based phosphor from the standpoint of emitting high-level stimuable emission. On the other hand, the stimuable phosphor used in the present invention is not limited to the above-described examples, and any phosphor which emits stimulated

emission when stimulating ray is irradiated thereon after being irradiated with radiation may also be used.

The grain size of the stimuable phosphor is preferably in a range from 1 to 15  $\mu\text{m}$ , more preferably in a range from 2 to 10  $\mu\text{m}$ . If the grain size is less than 1  $\mu\text{m}$ , the quantity of emitted light may decrease. If the grain size is greater than 15  $\mu\text{m}$ , the graininess may deteriorate. Both cases are not preferable.

[Binder]

A thermoplastic elastomer is favorably used as the binder. The thermoplastic elastomer preferably has a softening temperature or melting point of 30 to 150°C and also has an elastic modulus of 0.3 kgf/mm<sup>2</sup> or less (a thermoplastic elastomer having such properties will be hereinafter referred to as "specified thermoplastic elastomer"). An elastomer containing the above-described specified thermoplastic elastomer is preferably used as a principal component of the binder (preferably, at a ratio of 60% or greater of the binder). The specified thermoplastic elastomer is preferably used in a range from 30 to 100 % by weight based on the total weight of the elastomer, more preferably in a range from 60 to 100 % by weight, and most preferably in a range from 80 to 100 % by weight.

The softening temperature or melting point of the thermoplastic elastomer is preferably in a range from 30 to 120°C, more preferably in a range from 30 to 100°C. The softening temperature mentioned in the present invention is Vicat softening temperature.

The elastic modulus of the thermoplastic elastomer is preferably  $0.3 \text{ kgf/mm}^2$  or less, more preferably  $0.1 \text{ kgf/mm}^2$  or less. Further, a lower limit value of the elastic modulus is preferably set to be 0.001 or more.

The tensile strength of the thermoplastic elastomer is generally in a range from  $0.1$  to  $20 \text{ kgf/mm}^2$ , preferably in a range from  $1$  to  $15 \text{ kgf/mm}^2$ , and particularly preferably in a range from  $1$  to  $10 \text{ kgf/mm}^2$ . The tensile elongation percentage of the above-described specified thermoplastic elastomer is generally in a range from  $10$  to  $2000 \%$ , preferably in a range from  $100$  to  $1500 \%$ , and more preferably in a range from  $200$  to  $1500 \%$ .

Specific examples of the thermoplastic elastomer include polystyrene, polyolefine, polyurethane, polyester, polyamide, polybutadiene, ethylene vinyl acetate, polyvinyl chloride, natural rubber, fluorine-contained rubber, polyisoprene, chlorinated polyethylene, styrene-butadiene rubber, and silicon rubber. Among these examples, polyurethane, polyester, and polyolefine are preferably used, and polyurethane is particularly preferable.

As the binder, the above-described specified thermoplastic elastomer may be used alone, or as a mixture of two or more kinds of thermoplastic elastomer. Further, a mixture of two or more kinds of elastomer, comprised of the above-described specified thermoplastic elastomer and other elastomer, may also be used. Moreover, a polymer other than the thermoplastic elastomer (for example, an epoxy resin) may be mixed therewith. Particularly, the epoxy resin is

usually used to prevent occurrence of yellowing. In this case, polymers other than the thermoplastic elastomer are used at a ratio of less than 40% by weight based on the total weight of the binder.

A generally known cross linking agent can be added to the binder so that the above-described elastic modulus and tensile strength are each adjusted to a desired value. Examples of the cross linking agent which can be used include polyisocyanate, primary amine, secondary amine, and acid anhydride. The cross linking agent can be suitably selected based on the kind of elastomer or polymer used as the binder, desired properties, and the like. Further, the amount of the cross linking agent added may be suitably adjusted as well.

[Support]

Materials for a support can be arbitrarily selected from a group, for example, consisting of glass, a metallic plate, various materials used as supports for sensitized paper (or intensifying screen) in conventional radiography, and materials generally known as a support for a radiation image conversion panel. Examples of such materials include a plastic film such as cellulose acetate, polyester, polyethylene terephthalate, polyamide, polyimide, triacetate, or polycarbonate; a metal sheet such as aluminium foil or aluminium alloy foil; paper such as plain paper, baryta paper (photographic base paper), resin treated paper, pigment paper containing a pigment such as titanium dioxide, or paper formed by sizing polyvinylalcohol or the like; a plate or sheet of ceramics such as alumina, zirconia, magnesia,

and titania; and the like.

As well as a generally known radiation image conversion panel, in order to strengthen bonding of the support and the phosphor layer or to improve sensitivity or image quality (sharpness and graininess) of the radiation image conversion panel, the support can include, on the surface thereof at a side where the phosphor layer is provided, various layers which includes an adhesiveness imparting layer comprised of a polymer such as gelatin, a light reflection layer comprised of light reflecting substances such as titanium dioxide, gadolinium oxide, or the like, a light absorbing layer comprised of light absorbing substances such as carbon black, and the like. The configuration of these layers can be arbitrarily selected in accordance with the purpose and application of a desired radiation image conversion panel.

The support may be, as disclosed in JP-A No. 58-200200, formed in such a manner that micro irregularities are made on the surface thereof at a side which faces the phosphor layer (in a case in which the adhesiveness imparting layer, reflective light layer, or light absorbing layer is provided on the surface of the support at the side which faces the phosphor layer, which surface means the surface of any of these three layers), so as to improve the sharpness of an image to be obtained.

The thickness of the support is not particularly limited, but usually, it is preferably in a range from 75 to 300  $\mu\text{m}$ , more preferably in a range from 150 to 200  $\mu\text{m}$ .

(Protective layer)

In the radiation image conversion panel of the present invention, a protective layer may be provided on a surface of the phosphor layer, opposite to a side at which the phosphor layer abuts the support, so as to physically and chemically protect the phosphor layer in the same way as in an ordinary radiation image conversion panel.

The protective layer is preferably a transparent protective layer. Examples of material for the protective layer include: cellulose derivatives such as cellulose acetate and nitrocellulose; and synthetic polymers such as polymethylmethacrylate, polyvinylbutyral, polyvinylformal, polycarbonate, polyvinylacetate, vinyl chloride/vinyl acetate copolymer, and fluorine-based resin (for example, fluoro-olefine/vinyl ether copolymer).

The transparent protective layer can be formed by applying, onto the surface of the phosphor layer, a solution prepared by dissolving the above-described synthetic polymer in a suitable solvent. Further, a cross linking agent such as polyisocyanate can be used according to circumstances. Alternatively, the protective layer can be formed, for example, by a method in which a protective layer-forming sheet such as a plastic sheet comprised of polyethylene terephthalate, polyethylene naphthalate, polyethylene, polyvinylidene chloride, or polyamide; or a transparent glass plate is formed separately and bonded to the surface of the phosphor layer using suitable adhesives.

The thickness of the protective layer is not particularly

limited. Usually, it is preferably in a range from 0.1 to 20  $\mu\text{m}$ .

(Colored layer)

In order to improve the sharpness of an image to be obtained, the radiation image conversion panel of the present invention may include a colored layer, which absorbs stimulating ray but does not absorb light of stimulated emission, between any overlapping layers (see Japanese Patent Application Publication (JP-B) No. 59-23400).

(Edge covering layer)

In order to further improve conveying-resistant characteristics, particularly, impact resistant and contamination control, the radiation image conversion panel of the present invention may include an edge covering layer at an end (side surface portion) of at least one side of the radiation image conversion panel.

A coating for forming an edge covering layer is not particularly limited. For example, linear polyester or a polymer mixture of linear polyester and vinyl chloride/vinyl acetate copolymer disclosed in JP-A No. 62-3700, organic solvent-soluble fluorine based resin disclosed in JP-A No. 4-2998, and the like can be used. Further, a mixture comprised of a silicone based polymer and a polyisocyanate, of which details are disclosed in JP-A No. 7-140300, may also be used. The radiation image conversion panel in which an edge covering layer is formed by such coating allows achievement of extremely high-level conveying-resistant characteristics, particularly, impact resistance and contamination control.

(Manufacturing of radiation image conversion panel)



such as methyl acetate, ethyl acetate, or butyl acetate; ethers such as dioxane, ethyleneglycol monoethyl ether, ethyleneglycol monomethyl ether, and tetrahydrofuran; and mixtures thereof.

The coating liquid for forming the phosphor layer may include various additives, for example, a dispersing agent for improving dispersibility of a phosphor in the coating liquid, a plasticizer for improving bonding strength of the phosphor and a binder in a formed phosphor layer, and the like. Examples of the dispersing agent used for the above-described purpose include phthalic acid, stearic acid, caproic acid, and lipophilic surface active agent. Further, examples of the plasticizer include: phosphates such as triphenyl phosphate, tricresyl phosphate, and diphenyl phosphate; phthalate esters such as diethyl phthalate and dimethoxyethyl phthalate; glycolic acid esters such as glycolic acid ethylphthalylethyl, and glycolic acid butylphthalylbutyl; and polyesters of aliphatic dibasic acid and polyethylene glycol such as polyester of triethylene glycol and adipic acid, or polyester of diethylene glycol and succinic acid.

## (2) Formation of phosphor layer

The phosphor layer-forming coating liquids 1 and 2 thus prepared, which each contain a phosphor and a binder, are uniformly applied onto the surface of a sheet-forming temporary support and coating films of the coating liquids are thereby formed. The coating operation can be conducted by using an ordinary coating method, for example, a doctor blade, a roll coater, or a knife coater. Further, the temporary support can be arbitrarily selected from the same materials

as those for the above-described support.

The phosphor layer-forming coating liquids 1 and 2 were respectively applied onto separate temporary supports and dried, and thereafter, dried products were peeled from the temporary supports and phosphor sheets 1 and 2 were prepared as phosphor layers of the radiation image conversion panel. Accordingly, it is preferable that a mold releasing agent be in advance applied onto respective surfaces of the temporary supports so that formed phosphor sheets are easily peeled from the temporary supports.

### (3) Bonding of phosphor layer to support

The phosphor sheets 1 and 2 thus obtained were placed on the support in the order of the phosphor sheet 2 and the phosphor sheet 1, and were bonded to the support while being compressed (by thermo-compression bonding) preferably at a temperature higher than or equal to the softening temperature or melting point of the binder, and two-layered phosphor layer were thereby formed.

As a compressor used for the compression processing, generally known devices such as a calender roll and hot press can be used. For example, the compression processing using the calender roll is conducted by placing the above-described phosphor sheets on the support and passing them between rollers heated to a temperature higher than or equal to the softening temperature or melting point of the binder at a fixed speed. However, the compressor used in the present invention is not limited to the above-described devices, and any device by which the above-described phosphor sheets can be

compressed while being heated may also be used.

A pressure to be set during the compression processing is generally 50 kgw/cm<sup>2</sup> or more, preferably 200 to 700 kgw/cm<sup>2</sup>. A heating temperature (in a case of the compression processing using a calender roll, the temperature of each of the upper and lower rolls) is, as described above, generally set to be a temperature higher than or equal to the softening temperature or melting point of the binder, preferably a temperature higher than the softening temperature or melting point by 10 to 50 °C. Generally, upper and lower pressurizing members which apply pressure (in a case of the compression processing using a calender roll, upper and lower rolls) are preferably set at the same temperature. A feed speed in the compression processing using a calender roll is preferably set in a range from 0.1 to 5.0 m/minute.

#### (4) Formation of protective layer and edge covering layer

When necessary, a protective layer is formed on the surface of the phosphor layer and an edge covering layer is formed at an end (side surface portion) of at least one side of the radiation image conversion panel. The protective layer can be formed by a conventionally known method or the above-described method, and the edge covering layer can be formed by a conventionally known method.

The radiation image conversion panel of the present invention can thus be obtained.

## EXAMPLES

The present invention will further be described in detail with reference to the following examples, but it is not limited to these examples. In the examples given below, all "parts" indicate "parts by weight" as far as no particular explanation is given.

#### Example 1

##### (1) Preparation of upper-layer phosphor sheet

##### (Composition of upper-layer phosphor sheet)

Phosphor; BaFBr<sub>0.85</sub>I<sub>0.15</sub>: Eu<sup>2+</sup> (grain size: 8 μm) 1000 parts

Binder; 60 parts

; polyurethane elastomer (manufactured by Dainippon Ink & Chemicals, Inc.; trade name: Pandex T5265H [solid] 15% MEK solution)

; epoxy resin (manufactured by Yuka Shell Epoxy Co., Ltd.; trade name: EP1001 [solid])

; polyisocyanate (manufactured by Nihon Polyurethane Co., Ltd.; trade name: Colocate HX)

(A weight-mix ratio of the binder (polyurethane elastomer: epoxy resin: polyisocyanate) is 70:20:10.)

An optimum amount of MEK was added to the material having the above-described composition so that the viscosity becomes 30 Pa·s, and then dispersed and mixed by using a propeller mixer. As a result, a phosphor sheet-forming coating liquid having a viscosity of 30 Pa·s (25 °C) was prepared. This coating liquid was applied onto polyethylene terephthalate (temporary support; thickness: 190 μm) which is applied with a silicon-based mold releasing agent, and then

dried. Subsequently, the dried product was peeled from the temporary support and an upper-layer phosphor sheet (thickness: 140  $\mu\text{m}$ ) was obtained.

(2) Preparation of lower-layer phosphor sheet

A lower-layer phosphor sheet (thickness: 140  $\mu\text{m}$ ) was prepared in the same way as in the upper-layer phosphor sheet except that an amount of addition of the binder comprised of the composition of the upper-layer phosphor sheet was changed to 50 parts.

(3) Formation of reflective layer (undercoat layer)

(Composition of reflective layer)

Fine grains of gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ) (the grain size of grains which amount to 90% by weight of all grains is in a range from 1 to 5  $\mu\text{m}$ )

30 parts

Binder: soft acrylic resin (Cryscot P-1018GS: 20% solution;

manufactured by Dainippon Ink & Chemicals, Inc. 30 parts

Phthalate ester 3.5 parts

Conductive material: ZnO whisker 10 parts

Coloring agent: ultramarine blue 0.4 parts

An optimum amount of MEK was added to the material having the above-described composition, and then dispersed and mixed by using a propeller mixer. As a result, a reflective (undercoat) layer-forming coating liquid having a viscosity of 10 Pa·s (20  $^{\circ}\text{C}$ ) was prepared. Polyethylene terephthalate (support) having a thickness of 300  $\mu\text{m}$  was horizontally placed on a glass plate and the above-described undercoat layer-forming coating liquid was uniformly

applied onto the support, and thereafter, a coating film was dried and a reflective layer (thickness: 20  $\mu\text{m}$ ) was formed on the support.

#### (4) Formation of phosphor layer

The previously prepared upper-layer phosphor sheet and lower-layer phosphor sheet were placed on the reflective layer formed on the support in the order of the lower-layer phosphor sheet and the upper-layer phosphor sheet with surfaces thereof, at sides where these phosphor sheets are peeled from the temporary supports, facing each other, and then subjected to thermo-compression bonding. The thermo-compression bonding was continuously conducted by using a calender roll under the condition that a pressure is 500  $\text{Kg}/\text{cm}^2$ , the temperature of an upper roll is 90  $^{\circ}\text{C}$ , the temperature of a lower roller is 75  $^{\circ}\text{C}$ , and a feed rate is 1.0 m/minute. Due to the thermo-compression bonding, the reflective layer formed on the support and the phosphor sheets are completely bonded by fusion to each other, and a two-layered phosphor layer was formed. The thickness of the phosphor layer was made smaller by about 25 % and a filling factor of the phosphor thereby became greater.

#### (5) Formation of protective layer

(Composition of protective layer)

Fluorine-based resin: fluoroolefine/vinylether copolymer (Lumifron LF-504X (40 % solution), manufactured by Asahi Glass Co., Ltd.

50 parts

Cross linking agent: polyisocyanate (Olestar NP38-70S (70 % solution), manufactured by Mitsui Toatsu Chemicals, Inc.)

	9 parts
Lubricant: alcohol-denatured silicone (X-22-2809 (66 % solution), manufactured by Shin-Etsu Chemical Co., Ltd.)	0.5 parts
Catalyst: dibutyltindilaurate (KS1260, manufactured by Kyodo Chemical Co., Ltd.)	3 m parts

The material having the above-described composition was dissolved in an optimum amount of methyl ethyl ketone/cyclohexane (2/8, volume ratio) and a protective layer-forming coating liquid having a viscosity of 0.2 to 0.3 Pa·s was prepared. The protective layer-forming coating liquid was applied onto the above-described phosphor layer, and thereafter, subjected to heat treatment for 30 minutes at 120 °C so as to be thermally hardened, and then dried. As a result, a protective layer having a thickness of 3 µm was provided.

#### (6) Formation of edge covering layer

(Composition of edge covering layer)

Silicone-based polymer (polyurethane having polydimethylsiloxane units, Diaroma SP-3023 (15 wt% solution (solvent: mixed solvent of methyl ethyl ketone and toluene)), manufactured by Dainichiseika Colour & Chemicals Mfg. Co., Ltd.)	70 parts
Cross linking agent: polyisocyanate (Crossnate D-70 (50 wt% solution), manufactured by Dainichiseika Colour & Chemicals Mfg. Co., Ltd.)	3 parts

Yellowing inhibitor: epoxy resin (EP1001 [solid]; manufactured by Yuka Shell Epoxy Co., Ltd.)	0.6 parts
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Lubricant: alcohol-denatured silicone (X-22-2809 (66% solution),	
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manufactured by Shin-Etsu Chemical Co., Ltd.) 0.2 parts

The material having the above-described composition was added to 15 parts of methyl ethyl ketone and dissolved therein, and an edge covering layer-forming coating liquid was prepared. The edge covering layer-forming coating liquid was applied onto side surfaces of a panel comprised of the previously prepared support, undercoat layer, phosphor layer, and protective layer, and then dried completely at room temperature. As a result, an edge covering layer having a film thickness of 25  $\mu\text{m}$  was formed.

In such a manner as described above, a radiation image conversion panel of example 1 comprised of the support, undercoat layer, two-layered phosphor layer, protective layer, and edge covering layer was manufactured.

[Examples 2 to 5, Comparative examples 1 and 2]

Radiation image conversion panels of examples 2 to 5 and comparative examples 1 and 2 were each obtained by forming a two-layered phosphor layer as in example 1 except that the grain size of the phosphor, the amount of the binder, and the thickness of each phosphor sheet were changed to values shown in Table 1, which will be given later, in preparation of the upper-layer and lower-layer phosphor sheets.

[Evaluation]

The image qualities (the quantity of emitted light and the graininess) of each of images obtained from the radiation image conversion panels of examples 1 to 5 and comparative examples 1 and



2 were evaluated as follows. The results are shown in Table 1.

Each of the radiation image conversion panel thus prepared was irradiated with X-rays having a tube voltage of 80 KVp from the side of the protective layer, followed by scanning with He-Ne Laser light (having a wavelength of 632.8 nm) to thereby allow the phosphor to be excited. Light of stimulated emission emitted from the phosphor layer was received and converted into an electric signal, and the electric signal was reproduced by an image reproducing device and an image was obtained on a display device. The quantity of light of stimulated emission emitted from the phosphor layer at this time was measured, and a graininess (RM) noise in dosage of 10 mR was measured. In this measurement, a measuring device manufactured by Fuji Photo Film Co., Ltd. (trade name: FCR7000) was used.

TABLE 1

	Upper-layer phosphor sheet			Lower-layer phosphor sheet		
	Phosphor grain size ( $\mu\text{m}$ )	Amount of binder (parts)	Thickness ( $\mu\text{m}$ )	Phosphor grain size ( $\mu\text{m}$ )	Amount of binder (parts)	Thickness ( $\mu\text{m}$ )
Ex. 1	8	60	140	8	50	140
Ex. 2	8	70	140	8	50	140
Ex. 3	8	60	100	8	50	180
Ex. 4	8	60	180	8	50	100
Ex. 5	3	60	140	3	50	140
Comp. Ex. 1	8	50	140	8	50	140
Comp. Ex. 2	8	50	140	8	60	140

	Radiation image conversion panel	
	Light emission quantity (%)	Graininess noise ( $\times 10^{-2}$ )
Ex. 1	100	0.27
Ex. 2	98	0.25
Ex. 3	102	0.28
Ex. 4	100	0.26
Ex. 5	96	0.23
Comp. Ex. 1	100	0.33
Comp. Ex. 2	94	0.35

Notes: "Ex." means Example, and "Comp. Ex." means Comparative Example.

As can be seen from the results of Table 1, the graininess noise can be reduced by a multi-layered phosphor layer, in which the amount of a binder contained in an upper-layer phosphor layer is made larger, without decreasing the quantity of light emitted from a phosphor. As a result, a radiation image conversion panel having a desired S/N ratio can be obtained.

As described above, the present invention can provide a radiation image conversion panel having a sufficient quantity of light emitted from a phosphor and high graininess.

WHAT IS CLAIMED IS:

1. A radiation image conversion panel comprising at least two phosphor layers each containing a stimuable phosphor and a binder, wherein an amount (by weight) of the binder to the stimuable phosphor in uppermost phosphor layer of the phosphor layers is greater than that of the binder to the stimuable phosphor in any other phosphor layers.

2. A radiation image conversion panel according to claim 1, wherein the amount (by weight) of the binder to the stimuable phosphor in the uppermost phosphor layer is greater than that of the binder to the stimuable phosphor in any other phosphor layers by at least 0.5 wt%.

3. A radiation image conversion panel according to claim 1, wherein the amount (by weight) of the binder to the stimuable phosphor in the uppermost phosphor layer is greater than that of the binder to the stimuable phosphor in any other phosphor layers by 1 to 100 wt%.

4. A radiation image conversion panel according to claim 1, wherein the stimuable phosphor results a stimulated emission of a wavelength in the range of 300 to 500nm when the stimuable phosphor is irradiated with stimulating rays of a wavelength in the range of 400 to 900nm.

5. A radiation image conversion panel according to claim 1, wherein the stimuable phosphor is a phosphor selected from the group consisting of a bivalent europium-activated alkaline earth metal halide phosphor, a cerium-activated alkaline earth metal halide based phosphor, and a cerium-activated rare earth oxyhalide based phosphor.

6. A radiation image conversion panel according to claim 1, wherein the stimuable phosphor has a grain size ranging from 1 to 15  $\mu\text{m}$ .

7. A radiation image conversion panel according to claim 1, wherein the binder is a thermoplastic elastomer.

8. A radiation image conversion panel according to claim 7, wherein the thermoplastic elastomer includes at least one elastomer selected from the group consisting of polystyrene, polyolefine, polyurethane, polyester, polyamide, polybutadiene, ethylene vinyl acetate, polyvinyl chloride, natural rubber, fluorine-contained rubber, polyisoprene, chlorinated polyethylene, styrene-butadiene rubber, and silicon rubber.

## ABSTRACT OF THE DISCLOSURE

There is provided a radiation image conversion panel having a sufficient quantity of emitted light and high graininess. The radiation image conversion panel comprises a phosphor layer containing a stimutable phosphor and a binder. The phosphor layer is comprised of at least two layers, and an amount or weight of a binder to a stimutable phosphor in an uppermost layer of the phosphor layer is greater than that of a binder to a stimutable phosphor in other layer than the uppermost layer.

# BIRCH, STEWART, KOLASCH & BIRCH, LLP

## COMBINED DECLARATION AND POWER OF ATTORNEY

### FOR PATENT AND DESIGN APPLICATIONS

ATTORNEY DOCKET NO.

1982-0149P

PLEASE NOTE:  
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FOLLOWING:

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated next to my name; that I verily believe that I am the original, first and sole inventor (if only one inventor is named below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Insert Title:

RADIATION IMAGE CONVERSION PANEL

Fill in Appropriate  
Information -  
For Use Without  
Specification  
Attached:

the specification of which is attached hereto. If not attached hereto,

the specification was filed on \_\_\_\_\_ as

United States Application Number \_\_\_\_\_; and /or

the specification was filed on \_\_\_\_\_ as PCT

International Application Number \_\_\_\_\_; and was

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I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I do not know and do not believe the same was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months (six months for designs) prior to this application, and that no application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to this application by me or my legal representatives or assigns, except as follows.

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Insert Priority  
Information:  
(if appropriate)

→ Prior Foreign Application(s)

11-121930

(Number)

Japan

(Country)

April/28/1999

(Month/Day/Year Filed)

Priority Claimed

☒ Yes ☐ No

☐ Yes ☐ No

☐ Yes ☐ No

☐ Yes ☐ No

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(Application Number)

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I hereby appoint the following attorneys to prosecute this application and/or an international application based on this application and to transact all business in the Patent and Trademark Office connected therewith and in connection with the resulting patent based on instructions received from the entity who first sent the application papers to the attorneys identified below, unless the inventor(s) or assignee provides said attorneys with a written notice to the contrary:

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